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# Thermal Oxidation and Its Relation to Chemiluminescence from Polyolefins and Polyamides

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**Summary**: Chemiluminescence (CL) from oxidation of polypropylene, polyethylene and polyamide has been compared and kinetic parameters based on the simplified kinetic scheme involving both bimolecular decomposition of hydroperoxides as an initiating event and correction for the oxidation spreading were determined. Induction times of oxidation determined from the autocatalytic shape of chemiluminescence intensity–time runs increase with an increasing initial molar mass of polypropylene within low molar masses up to 180 kDa regardless of the route of the polypropylene synthesis. The more complex chemiluminescence patterns in case of polyamides may be related with an increase of initially present defect structures including the terminal amino groups.

**Keywords**: chemiluminescence; degradation; polyamides; polyolefins; stabilization

## Introduction

The oxidation of any organic material is accompanied by a very weak light emission which is obviously related to the rate of the process, however, the relation is not usually straightforward and has to be examined for any particular case. As early as in 1961 and 1964 Ashby [1] and Schard [2] pointed out that different CL intensity – time patterns exist for the series of the most frequent polymers and that there is a necessity of better understanding the CL phenomenon. Some polymers like polypropylene, polyethylene and polyamides exhibit an autocatalytic increase of the intensity of the light emission accompanying the oxidation, which is apparently coincident with autocatalytic character of the oxidation process; some give only steady decay of the light intensity

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from an initial value. After years of a relatively active study of the CL phenomenon and its applicability in polymer oxidation some qualitative mechanistic findings may be summarized as follows [3]:

The signal intensity is determined by the quality of the polymer, by the character of its terminal groups, by the extent of previous oxidation and thermo and/or photo-oxidation history of the polymer sample expressed in concentration of hydroperoxides, carbonyl groups or other oxidized structures. The extent of oxidation corresponds to resulting mechanical properties of the polymer and to the average molar mass and its distribution. The ratio of amorphous/crystalline regions and tacticity of the polymer may affect the CL intensity – time patterns significantly.

The signal intensity is related to the sum of rates of initiating events generating free radicals, however, the contribution of respective initiating events to the total CL intensity may vary. The parallel formation of potential light emitters like excited carbonyl groups, singlet oxygen, etc. is beneficial for the increase of quantum yield of chemiluminescence. Increasing temperature and concentration of oxygen in the atmosphere surrounding the oxidized sample lead to an increase of the signal intensity. Chain breaking antioxidants and peroxide decomposers in polymers suppress the signal intensity until they are depleted in the oxidation process. Pre-oxidized polymers give an appreciable light emission at elevated temperature in nitrogen, which may come from the fast decomposing peroxidic structures.

In the classical Boland – Gee scheme of hydrocarbon oxidation involving initiation,

| | |
|---|---|
| 1/ $PH \rightarrow P^{\cdot}$ | $w_i$ |
| 2/ $P^{\cdot} + O_2 \rightarrow PO_2^{\cdot}$ | $k_2$ |
| 3/ $PO_2^{\cdot} + PH \rightarrow POOH + P^{\cdot}$ | $k_3$ |
| 4/ $POOH \rightarrow PO^{\cdot} + {}^{\cdot}OH$ | $k_{mono}$ |
| 5/ $2\,POOH \rightarrow PO_2^{\cdot} + PO^{\cdot} + H_2O$ | $k_{bi}$ |
| 6/ $PO^{\cdot} \rightarrow$ ketone $+ P^{\cdot}$ | $k_4$ |
| 7/ $PO^{\cdot}\,({}^{\cdot}OH) + PH \rightarrow POH\,(H_2O) + P^{\cdot}$ | $k_5$ |
| 8/ $2\,PO_2^{\cdot} \rightarrow POH + \text{ketone}^{*} + O_2^{*}$ | $k_6$ |
| 9/ $PO_2^{\cdot} + P^{\cdot} \rightarrow POOP$ | $k_7$ |
| 10/ $2\,P^{\cdot} \rightarrow P-P$ | $k_8$ |
| 11/ $PO_2^{\cdot} + SH \rightarrow$ products | $k_{inh}$ |
| 12/ $POOH + D \rightarrow$ products | $k_d$ |

propagation and termination of free radical chain process, CL is assumed to arise in step 8), which schematically denotes the disproportionation of secondary or primary peroxyl radicals. In the case of hydroperoxide decomposition in a micro-domain, where its concentration is significantly above the average value, we also suspect the step 5), which is bimolecular decomposition of hydroperoxides. Formally it may be identified with explosion-like process potentially yielding excited particles as well. Ketone$^*$ and $O_2^*$ are excited triplet states of ketone group and singlet oxygen, respectively. They are converted to the ground state either in a luminous way:

$$\text{ketone}^* \rightarrow \text{ketone} + h\nu$$
$$O_2^* \rightarrow O_2 + h\nu$$

or as heat dissipated in collisions.

One should be aware of the fact that only a very small part of excited states is converted to the ground state with the emission of the light, the prevailing part is quenched in a non-luminous way. This is a pre-requisite of more or less complex relation of observed CL intensity with the rate of initiation. Deconvolution of the respective initiation mechanism from CL - time runs may be rather difficult and sometimes impossible without a use of complementary methods. From the scheme of non-inhibited oxidation, assuming that chemiluminescence arises only in disproportionation of secondary or primary peroxyl radicals (step 8), one can propose that:

$$w_i + k_{mono}[POOH] + k_{bi}[POOH]^2 = k_6\,[PO_2^{\cdot}]^2 \approx I_{CL},$$

where $I_{CL}$ is the intensity of chemiluminescence. If the initiation route is governed predominantly by the decomposition of hydroperoxides, i.e. $k_{mono}[POOH] + k_{bi}[POOH]^2 >> w_i$, the isothermal autocatalytic pattern of CL will be observed during polymer oxidation, while the CL intensity will decay steadily from some intial value for $k_{mono}[POOH] + k_{bi}[POOH]^2 << w_i$ .

In the present paper we compare CL intensity – time runs for the oxidation of polypropylene, polyethylene and polyamide 6 (or polyamide 66) which are typical representatives of an autocatalytic increase of chemiluminescence intensity in time. However, the latter two polymers show more complex behavior, giving two mutually superimposed autocatalytic waves of chemiluminescence intensity runs.

## Experimental

The chemiluminescence device Lumipol 2 was used for chemiluminescence measurements. The instrument was designed and manufactured at the Polymer Institute, Slovak Academy of Sciences, Bratislava, Slovak Republic. Lumipol 2 has the level of discrimination 2 counts/s at 40 °C. A polymer film (2-3 mg) having a diameter of 6 mm, or fine polymer powder, was placed on the aluminium pan of the diameter 9 mm to the oven of chemiluminescence device. Oxygen gas (flow 3.4 l/h) passed through the reactor during the measurement.

Polypropylenes were synthesized at the Institute of Science and Technology of Polymers, Madrid. Unstabilised polyamide 6,6 (Radilon A), containing only a small amount of phosphate (several ppm) as synthesis catalyst, and less than 0.5% weight residual oligomers, was kindly supplied by Radicinovacips SpA (Chignolo d'Isola, Italy). Polyethylene was Marlex 55180, free of stabilisers.

## Results and Discussion

### *Kinetic analysis chemiluminescence – time runs*

In our previous papers [3-6] we showed that the isothermal CL runs can be well fitted by the eq. 1)

$$I = \frac{A\exp(-k_1 t)}{[1 + Y\exp(-k_2 t)]^2} \qquad 1)$$

where Y is positive for the case of oxidation having the sigmoidal shape and negative for the case of oxidation showing the monotonous decay of chemiluminescence. The advantage of the equation above lies in its direct relation to the oxidation process.

It was formulated assuming the bimolecular reaction of polymer hydroperoxides as the initiation step of the reaction scheme extracted from the more general scheme in the Introduction:

$$
\begin{aligned}
&2POOH \xrightarrow{k_{bi}} PO_2^{\cdot} + PO^{\cdot} + H_2O \\
&PO^{\cdot} + PH \xrightarrow{k} POH + P^{\cdot} \\
&P^{\cdot} + O_2 \xrightarrow{k_2} PO_2^{\cdot} \\
&PO_2^{\cdot} + PH \xrightarrow{k_3} POOH + P^{\cdot} \\
&2PO_2^{\cdot} \xrightarrow{k_6} products
\end{aligned}
$$

Here we assume that the transfer reaction of alkoxyl radicals $PO^{\cdot}$ to polymer PH is considerably faster than the corresponding reaction of peroxyl radicals so that the alkoxyl radicals concentration can be neglected compared to that of peroxyl radicals. The Differential equations for concentrations of alkyl radicals and peroxyl radicals were converted to algebraic ones using the Bodenstein principle of steady state. For the time changes of hydroperoxide concentration [POOH] we ultimately obtain eq. 2.

$$[POOH] = \frac{X}{1 + Y\exp(-k_2 t)} \qquad 2)$$

where $X = [POOH]_{\infty}$, $Y = \dfrac{[POOH]_{\infty} - [POOH]_0}{[POOH]_0}$

$$[POOH]_{\infty} = \frac{k_4[PH]}{2\sqrt{k_6 k_{bi}}} \text{ and } k_2 = k_4[PH]\sqrt{\frac{k_{bi}}{k_6}}$$

Having in mind the final goal to find an optimum fit with experimental runs we have postulated the relation between the CL intensity and time function F(t) so that it is the product of two terms. The first term represents the rate of hydroperoxide concentration changes. The second term, S(t), is the correction for the decay of the CL intensity when crossing the maximum, which is not so fast in experiments as it should correspond to the constant $k_2$ (See eq.4) .

$$I = \mu F(t) = \mu\left(\frac{d[POOH]}{dt}\right)S(t) \qquad 3)$$

(Proportionality constant μ is the yield of chemiluminescence.)

According to eq. 2 $\frac{d[POOH]}{dt} = \frac{k_2 XY \exp(-k_2 t)}{[1 + Y \exp(-k_2 t)]^2}$ 4)

when compared to the oxidation of uniform (liquid) medium from which we monitor the intensity of the light emission from a well defined surface, where all concentrations are well equilibrated, in solid polymers the situation is usually more complex. The diffusion of macromolecules is restricted and limits itself to polymer segments only. It may happen that the oxidation will start incidentally at some surface sites of the polymer from which it then spreads to the whole sample [7]. The surface emitting the light thus increases and so does the light of emission. The correction function S(t) takes such a possibility into account. In the first approximation we have expressed the function S(t) by an exponential rise as follows.

$$S(t) = S_0 \exp(rt) \qquad 5)$$

where $S_0$ is the initial surface where the start of oxidation is potentially the most probable because of accumulation of different defect sites and r is the rate constant of oxidized surface spreading.

By combination of eqs. 3, 4 and 5 we finally obtain the analytical expression 1), in which $A = \mu k_2 XYS_0$ and $k_1 = k_2 - r$.

Some theoretical runs of CL intensity for a set of parameters: A=20000, $k_1 = 5\ 10^{-6}\ s^{-1}$, $k_2 = 1\ 10^{-4}$ and several Y parameters are shown in Fig. 1. It can be seen that the induction time for the advanced stage of oxidation is determined not only by the corresponding rate constants but also by parameter Y, which is the ratio of maximum (at infinity time of the process) $[POOH]_\infty$ and initial concentrations of hydroperoxides $[POOH]_0$ reduced by 1. While the maximum concentration of hydroperoxides is determined by kinetic parameters and at a given temperature it should be constant, the initial concentration of hydroperoxides should be considered as the scale of the polymer quality including all other defect structures in the polymer due to processing, reactions of catalyst residuals, etc., which are converted to hydroperoxides. The higher the concentration of these defect structures is the lower the value of Y is. Provided that the defect structures predominate the maximum concentration of hydroperoxides kinetically attainable (Y<0), we face the case of steady decay of chemiluminescence intensity (See the decay curve in Fig. 1 for

A=1000, $k_l$=5 $10^{-6}$ $s^{-1}$, $k_2$=1 $10^{-4}$ $s^{-1}$ and Y= -0.8). This may happen when, for example, the rate constant $k_4$ of the transfer reaction of peroxyl radicals to a polymer chain is very low and thus the lengths of the kinetic chains are rather short.

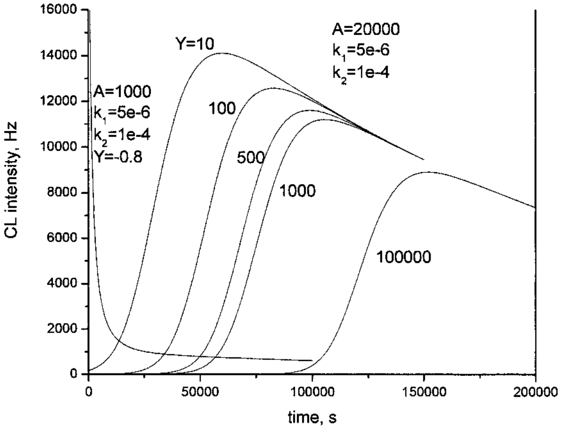

Figure 1. Theoretical runs of chemiluminescence intensity derived from eq. 1 for different values of parameters Y

## ***Experimental chemiluminescence intensity – time runs for non-stabilized and stabilized polypropylene***

The experimental runs of chemiluminescence intensity in time for polypropylenes, prepared by Ziegler Natta and metallocene catalysts, having different properties including molar mass, the degree of isotacticity, etc., are shown in Fig. 2. The temperature of the experiment was 100 °C. From Fig. 2, the dependence on molar mass becomes quite obvious. The higher the molar mass, the higher is the induction time and lower is the maximum chemiluminescence intensity.

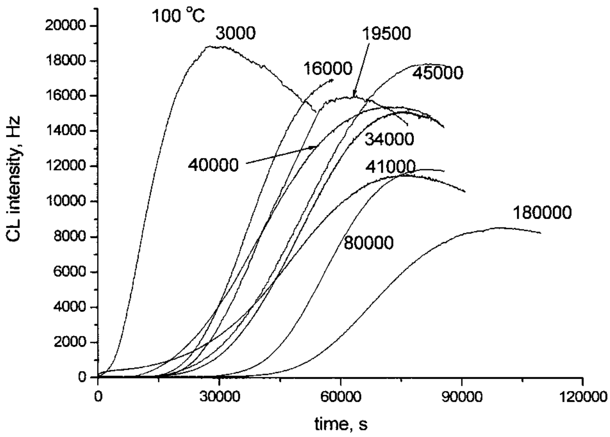

Figure 2. Experimental runs of chemiluminescence intensity – time for oxidation of powders of polypropylene (oxygen, 100 °C) – See also Table 1

The perfect fit of eq. 1 to experimental runs of CL from oxidized polypropylene was already demonstrated in our earlier papers [4,5]. Here we present parameters of the eq. 1 derived from such a fit (Table 1), corresponding to the series of experiments represented in Fig. 2.

It is of interest that parameter Y which is the scale of the concentration of defect structures in the polymer correlates well with the extent of isotacticity of the polymer (Fig. 3). The lowest concentration of the defect structures is in the polymer containing the highest isotacticity. 100% of isotactic structures from the mixture of isotactic, syndiotactic and atactic structures renders to polypropylene also the highest stability as seen from the induction times of oxidation (Fig. 4) and from rate constants of the fast decomposing peroxides (Fig. 5). Induction times were determined from the intercept of the straight line of maximum slope crossing the inflexion point of the CL run and time axis.

The conception of defect structures introduced through the term Y of eq. 1 may also be applicable to polypropylene stabilized by antioxidants. In Fig. 6 we see an example of the addition of

Table 1. Parameters of respective experimental runs and the fit by eq. 1 for oxidation of different polypropylenes (metallocene and Ziegler Natta) (powder, 3 mg) in oxygen at 100°C

| Molar mass | % of isotacticity | $I_{max}$ | $t_{ind}$ | $(d[\frac{I}{I_{max}}]/dt)_{max}$ * $10^5$ | Y | $k_1 * 10^6$ | $k_2$ x *$10^5$ |
|---|---|---|---|---|---|---|---|
| Daltons | | Hz | s | $s^{-1}$ | | $s^{-1}$ | $s^{-1}$ |
| 3000 | 84.9 | 18806 | 4146 | 6.2 | 6.2 | 9.2 | 19 |
| 16000 | 86 | 17087 | 23639 | 3.6 | 46.1 | - | 12 |
| 19500 | 86.6 | 16027 | 25165 | 3.23 | 49.2 | 20 | 10 |
| 34000 | 92.5 | 15113 | 30990 | 2.92 | 47.3 | 10 | 8 |
| 40000 * | 76.6 | 15417 | 19952 | 2.63 | 15.0 | 5.4 | 8 |
| 41000 | 89.4 | 11456 | 23661 | 2.48 | 16.3 | 20 | 6 |
| 45000 * | 82.2 | 17952 | 29046 | 2.46 | 28.5 | 4.4 | 8 |
| 80000 * | 100 | 11871 | 41290 | 3.61 | 274.1 | 6.4 | 11 |
| 180000 * | 100 | 8568 | 50476 | 2.78 | 240.9 | 5.2 | 9 |

*Ziegler Natta polypropylenes

x rate constant of fast decomposing peroxides in polypropylene at 100°C is 8.7 $10^{-5}$ $s^{-1}$, rate constant of slow decomposing peroxides in polypropylene at 100 °C is 2.4 $10^{-6}$ $s^{-1}$ [9,10]

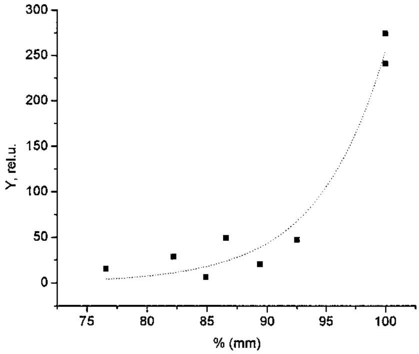

Figure 3. The plot of the parameter Y from eq. 1 on the extent of isotacticity as determined by FTIR measurements

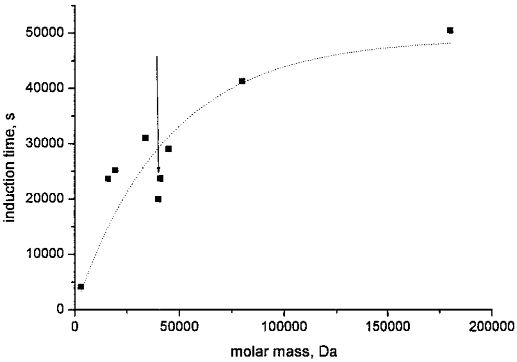

Figure 4. The plot of the induction times from Fig. 2 versus molar mass of metallocene and (left from the arrow) Ziegler-Natta polypropylenes

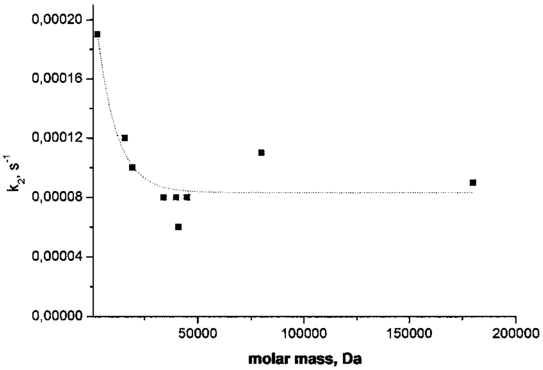

Figure 5. The plot of the rate constant $k_2$ of eq. 1 determined from experimental runs of oxidation of polypropylene from Fig. 2

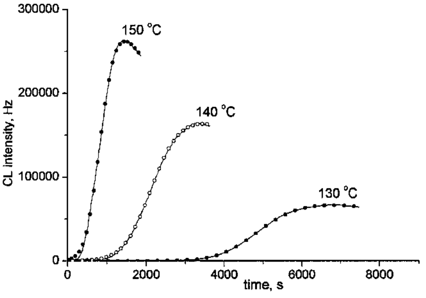

Figure 6. Chemiluminescence runs for oxidation (oxygen) of polypropylene stabilized with 0.1 wt.-% of Irganox 1076. Lines are experimental records, points denote theoretical runs corresponding to the fit of experiment by eq. 1

0.1 % wt of hindered phenol Irganox 1076 to polypropylene supplied from another source (Chemie Linz, Austria). The presence of antioxidant increases the value of Y significantly indicating again that Y is the main factor determining the induction time of oxidation. It appears as though the concentration of defect structures in the polymer contributing to the initiation of oxidation is considerably reduced by the presence of antioxidant. It is of interest that the presence of Irganox 1076 also brings about the reduction of the rate constants $k_2$ and $k_1$ (Table 2). It is to be borne in mind that the constant $k_2$ coincides numerically with the rate constant of hydroperoxide decomposition in the advanced stage of oxidation.

Table 2. Parameters of eq. 1 for chemiluminescence runs of oxidation of polypropylene stabilized with 0.1 wt. % of Irganox 1076

| Temperature | A | Y | $10^5 * k_1$, | $10^3 * k2$, |
|---|---|---|---|---|
| °C | Hz | | $s^{-1}$ | $s^{-1}$ |
| 130 | 132 826 | 840.4 | 9 | 1.5 |
| 140 | 286 546 | 54.98 | 14 | 2.15 |
| 140* | 62 843 | 5.51 | 17 | 3.9 |
| 150 | 465 570 | 17.69 | 34 | 4.13 |

*pure polypropylene

### ***Comparison of chemiluminescence runs during oxidation of polypropylene, polyethylene and polyamides***

On plotting chemiluminescence courses for the oxidation of the above three polymers at 140 °C we see that pure polypropylene attains the advanced stage of oxidation first, then followed by PA 66 and finally low density polyethylene (LD PE) (Fig. 7). On experimental runs of CL intensity – time of the two latter polymers, however, two well distinguished waves (I and II) are noticed. The initial intensity of CL accompanying the oxidation of polyamide 66 is, moreover, considerably higher than those of polypropylene (PP) and polyethylene. In one of our last papers [8] we have expressed an idea that this initial level of CL intensity corresponds to a faster oxidation of the terminal amino groups in polyamide 66. Regardless of the existence of two waves for the description of the kinetics of the process we have again used the eq.1 (Table 3). We see that the lowest concentration of defect structures (the highest Y) is found in polyethylene (Y=13.7), then in polypropylene (Y=5.31), while the highest concentration of defect structures exists in polyamide 66 (Y=1.83). This is probably due to the existence of terminal amino groups in the latter, which are potential sites of initial oxidizability. On the other hand, the rate constants $k_2$ are the highest for polypropylene, where oxidation occurs via tertiary hydroperoxides. The $k_2$ for polyamide 66 is one order of magnitude lower (oxidation takes place presumably via secondary hydroperoxides in the vicinity of the nitrogen of the amino group) and the lowest $k_2$ value was for the oxidation of polyethylene (oxidation occurs via secondary hydroperoxides).

Two-stage oxidation of polyethylene apparently disappears at temperatures below 130 °C (Fig. 8) and eq. 1 then describes the oxidation process very well. Parameters of the fit of CL from polyethylene at different temperatures are in Table 4. According to the definition of a respective term the higher values Y at lower temperatures correspond with higher maximum concentrations of hydroperoxides. The error brought about by application of eq. 1 to two waves reflects itself in a decrease of the rate constants $k_2$ and $k_1$ between 130 and 140 °C from the expected sequence.

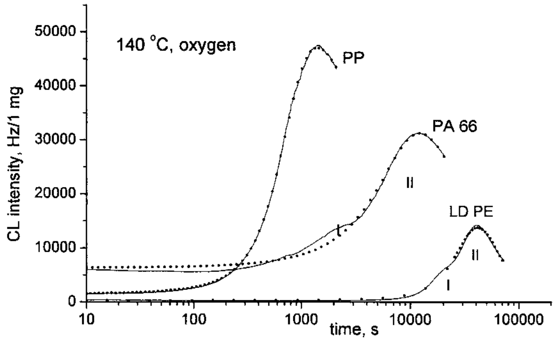

Figure 7. Comparison of chemiluminescence intensity – time runs accompanying the oxidation of polypropylene, polyamide 6 and low-density polyethylene at 140 °C. Lines are experimental runs, points are theoretical fits by eq. 1

The effect of some salts (200 ppm) on polyamide 66 is shown in Fig. 9. The fit of experimental runs by eq. 1 again yields quite a good fit. However, the Y values convert to negative values when $CuCl_2$ is added. $CuCl_2$ performs a strong antioxidation action (Table 5).

Table 3. Parameters of eq. 1 for chemiluminescence intensity – time runs accompanying oxidation (oxygen) of polypropylene, polyethylene and polyamide 6 at 140 °C

| Polymer | A | Y | $10^5 * k_1$ | $10^4 * k_2$ |
|---|---|---|---|---|
| | Hz | | $s^{-1}$ | $s^{-1}$ |
| polypropylene | 62 843 | 5.51 | 17 | 39 |
| polyamide 6 | 50 945 | 1.83 | 3 | 2.8 |
| polyethylene | 66 686 | 13.57 | 3 | 1.1 |

Table 4. Parameters of eq. 1 for chemiluminescence kinetics for oxidation of polyethylene

| Temperature | A | Y | $10^6 * k_1$ | $10^6 * k_2$ |
|---|---|---|---|---|
| °C | Hz | | $s^{-1}$ | $s^{-1}$ |
| 110 | 354 127 | 150.5 | - | 7.8 |
| 120 | 71 725 | 60 | 9.5 | 30 |
| 130 | 39 563 | 34 | 10 | 50 |
| 140 | 66 686 | 13.57 | 30 | 110 |
| 150 | 39 077 | 8.4 | 20 | 280 |

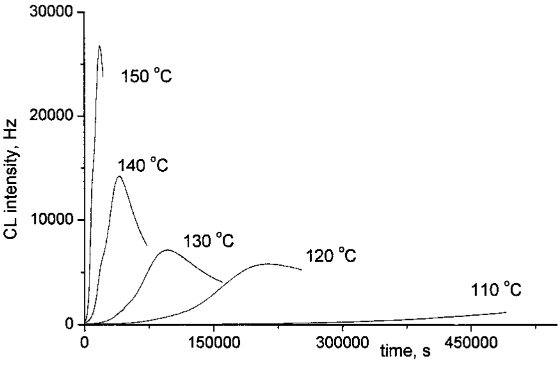

Figure 8. Chemiluminescence intensity runs accompanying the oxidation (oxygen) of low-density polyethylene

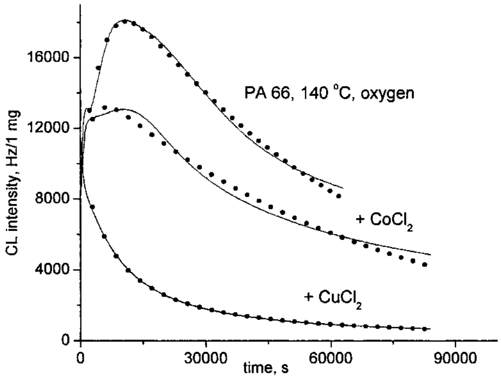

Figure 9. Chemiluminescence intensity – time runs for oxidation of polyamide 66 (oxygen) at 140°C in the presence of 200 ppm of some salts

Table 5. The parameters of eq. 1 for chemiluminescence runs accompanying the oxidation of polyamide 66 (PA 66) at 140 °C

| System | A<br>Hz | Y | $10^5 * k_1$<br>$s^{-1}$ | $10^4 * k_2$<br>$s^{-1}$ |
|---|---|---|---|---|
| PA 66 pure | 23 263 | 0.535 | 2 | 2.5 |
| PA 66 + $CoCl_2$ | 15 097 | 0.227 | 2 | 3.8 |
| PA 66 + $CuCl_2$ | 1 397 | -0.631 | 1 | 0.3 |

The rate constants $k_2$ of PA66 + $CuCl_2$ are almost one order of magnitude lower than those for pure polyamide 66. Accordingly, $CoCl_2$ acts as a pro-oxidant.

## Conclusions

The kinetics of chemiluminescence intensity – time runs may well be fitted by eq. 1 in the case of polypropylene and polyethylene provided that both polymers give a single autoaccelarating increase of the light emission. Oxidation of polyethylene above 130 °C and polyamides is accompanied typically by two waves chemiluminescence kinetics. From the kinetic equation the concentration of defect structures initially present in a polymer are related to the initial concentration of hydroperoxides. Kinetic parameters found from eq. 1 are well related to the rate constants of hydroperoxides decomposition during polymer oxidation.

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